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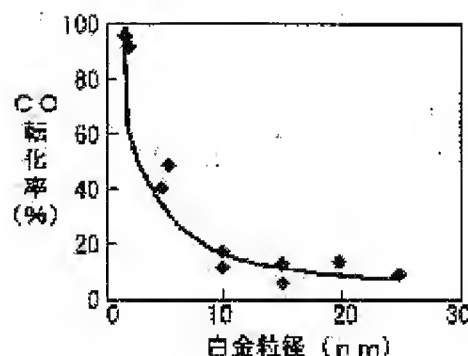
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(54) ORDINARY TEMPERATURE CATALYST

(57)Abstract:

PROBLEM TO BE SOLVED: To produce an ordinary temperature catalyst which is activated at ordinary temperature below 50°C so that it can decompose and remove environmentally pollution load materials such as CO, amines and formaldehyde.

SOLUTION: This ordinary temperature catalyst is obtained by carrying a noble metal on an oxide with introduced oxygen deficiency, and $\geq 90\%$ of the noble metal is carried in the form of fine particles of ≤ 2 nm particle diameter. Active oxygen contained in the oxygen deficiency reacts with environmentally pollution load materials adsorbed on the surface of the catalyst at ordinary temperature below 50°C to oxidize and decompose the materials. Though the active oxygen is consumed by the reaction, gaseous oxygen contained in the air is incorporated into the catalyst and becomes active oxygen, which reacts further with environmentally pollution load materials. Since the noble metal is carried as the fine particles, numerous active sites are present and the catalyst has very high activity at ordinary temperature below 50°C.



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CLAIMS

[Claim(s)]

[Claim 1]An ordinary temperature catalyst which supporting the precious metals to an oxide in which an oxygen deficiency was introduced, and supporting with a particle state with a particle diameter of 2 nm or less as for these the not less than 90% of precious metals.

[Claim 2]The ordinary temperature catalyst according to claim 1 as which said oxide is chosen from a transition metal oxide and a rare earth oxide and which is a kind at least.

[Claim 3]Said transition metal oxide A zirconium, iron, manganese, cobalt, nickel, The ordinary temperature catalyst according to claim 2 which is chosen from an oxide of copper, chromium, molybdenum, and niobium, as which it is a kind at least and said rare earth oxide is chosen from an oxide and the Cellier zirconia of cerium, yttrium, neodymium, praseodymium, and samarium and which is a kind at least.

[Claim 4]The ordinary temperature catalyst according to claim 1 characterized by a thing for which said precious metals are chosen from Pt, Pd, Rh, Ir, Ru, and Au, and which is a kind at least.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates, for example to the ordinary temperature catalyst which can carry out decomposition removal of the environmentally harmful substances, such as carbon monoxide (CO), hydrocarbon (HC), aldehyde, ethylene, and ammonia, easily at ordinary temperature (room temperature) 50 ** or less.

[0002]

[Description of the Prior Art]For example, isolation formaldehyde may be contained in the coat currently painted by plywood adhesive or furniture, and it is gradually emitted into the atmosphere. From the industrial commodity using adhesives and the paint which use formaldehyde as a raw material, formaldehyde occurs with degradation. This formaldehyde has a pungent smell and is pointed out as one of the causative agents of sick house syndrome. Therefore, in the housebuilder, before handing over to the after-construction chief mourner of a residence, are performing efforts to age the inside of a residence and reduce formaldehyde concentration, but. It cannot say that the reference value of Ministry of Health and Welfare is not necessarily fulfilled only by aging, but the further reduction of the formaldehyde concentration in the air is called for.

[0003]Then, the method of using adsorption material, such as a method of using ozone or activated carbon, and zeolite, as a method of removing the environmentally harmful substance in the air is performed widely. For example, what stored adsorption material in the container which can circulate air as a deodorant which is put on a refrigerator, a closet, a shoe cupboard, etc. and is deodorized is marketed. The air cleaner having adsorption material or a photocatalyst, etc. are known.

[0004]In order that the ethylene contained in the air may promote the physiological function of garden stuff and may advance ripening and senescence, it is considered that the freshness of garden stuff falls with ethylene. Therefore, removal of the ethylene from the atmosphere is effective in the freshness keeping of garden stuff, and the method which is made to disassemble ethylene with ozone or hydrogen peroxide, or has ****ed the adsorption treatment of the ethylene enough and carries out it is proposed.

[0005]For example, a photocatalyst and an ultraviolet ray source are arranged in the storage container which accommodates fresh vegetables, and the device which carries out decomposition removal of the gas harmful to the freshness keeping of fresh vegetables, such as ethylene and acetaldehyde, by a photocatalyst effect is indicated by JP,7-260331,A.

[0006]For example, the catalyst which supported the precious metals to the carrier including zirconia or Seria is indicated by JP,10-296087,A. According to this catalyst, oxidative degradation of the trimethylamine can be carried out by using at the temperature of about 200 **.

[0007]And as the catalyst which oxidizes CO and HC, or a catalyst which returns NO_x, the catalyst which supported the precious metals is known by carriers, such as alumina, and it is widely used for them as a catalyst for emission gas purification, etc.

[0008]

[Problem(s) to be Solved by the Invention]However, in the method of using ozone, in order to make the effect of ozone reveal, the ozone level which exceeds a restriction value is required, and also after removing an environmentally harmful substance, a possibility that ozone may remain is. Therefore, it is not practical that the catalyst for processing residual ozone is needed etc.

[0009]It is difficult to adsorb the environmentally harmful substance in the air by the method of adsorbing and removing exceeding the adsorption capacity of adsorption material by adsorption material, and before the amount of adsorption is saturated, it is necessary to exchange adsorption material.

[0010]And in the method of using a photocatalyst, when the artificial source used as the excitation source of a photocatalyst is required and a photocatalyst is always irradiated with a light source, the electrical charges which operate a light source are also needed, and it is high in cost.

[0011]In the method of furthermore using a catalyst, temperature must be raised to the activation temperature of the precious metals, and the catalyst activated at ordinary temperature 50 ** or less is not known for it yet.

[0012]This invention is made in view of such a situation, and is a thing.

The purpose is to provide the catalyst which is activated at the ordinary temperature of ** and can carry out decomposition removal of the environmentally harmful substances, such as CO, amines, and formaldehyde.

[0013]

[Means for Solving the Problem]The feature of an ordinary temperature catalyst of this invention which solves an aforementioned problem supports the precious metals to an oxide in which an oxygen deficiency was introduced, and there are the precious metals in the not less than 90% being supported with a particle state with a particle diameter of 2 nm or less.

[0014]As this oxide, a kind is [choose / out of a transition metal oxide and a rare earth oxide] desirable in it being few, and a transition metal oxide, It is a kind at least and thing of a rare earth oxide as which it is chosen out of an oxide of Zr, Fe, Mn, Co, nickel, Cu, Cr, Mo, and Nb,

which is chosen from an oxide of Ce, Y, Nd, Pr, and Sm and $\text{CeO}_2\text{-ZrO}_2$ and which is a kind at least is desirable. As the precious metals, Pt, Pd, Rh, Ir, Ru, and Au are desirable, and especially Pt is desirable.

[0015]

[Embodiment of the Invention]The ordinary temperature catalyst of this invention is supporting the precious metals to the oxide in which the oxygen deficiency was introduced. An oxygen deficiency means the state with very high activity where a part of oxygen which forms the oxide ****ed, and means a state with less molar quantity of oxygen united as an oxide than default value. For example, since it is in the state where CeO_2 does not have an oxygen deficiency in the case of Ce oxide, if an oxygen atom is less than a double mol to Ce atom, it will be said that the oxygen deficiency is introduced.

[0016]Active oxygen is contained in this oxygen deficiency, and this active oxygen reacts to the environmentally harmful substance which stuck to the catalyst surface at ordinary temperature 50 ** or less, and carries out oxidative degradation of the environmentally harmful substance. Although the active oxygen contained in the catalyst is consumed by a reaction with an environmentally harmful substance, the oxygen gas contained in the air is incorporated into a catalyst, it becomes active oxygen, and it reacts to an environmentally harmful substance further. Thus, when oxidation reaction advances catalytically, oxidative degradation of the environmentally harmful substance can be carried out, and it can be removed.

[0017]The ordinary temperature catalyst of this invention is supporting the precious metals to the oxide in which this oxygen deficiency was introduced. The activity of the oxide itself is improved by the oxygen deficiency and, as a result, the adsorptivity to the precious metals of an environmentally harmful substance becomes weaker. The activity of the precious metals increases by this and oxidation reaction of an environmentally harmful substance advances using the active oxygen activated via the oxygen-deficiency part.

[0018]For example, CO oxidizes by active oxygen and serves as CO_2 , and formaldehyde (HCHO) or ethylene (C_2H_4) oxidizes, it is set to CO_2 and H_2O and is detoxicated.

[0019]Furthermore, the not less than 90% of the precious metals are supported with the ordinary temperature catalyst of this invention in the particle state with a particle diameter of 2 nm or less. Since the precious metals are supported with the state detailed in this way, there is very much the active spot and the activity in ordinary temperature 50 ** or less is very high.

[0020]Although what is necessary is just to be able to introduce an oxygen deficiency, as an oxide Zr, The oxide of at least a kind of rare earth element chosen from the oxide or Ce, Y, Nd, Pr, and Sm of at least a kind of transition metal chosen from Fe, Mn, Co, nickel, Cu, Cr, Mo, and Nb is preferred. A kind of these may be sufficient and two or more kinds can also be used together.

[0021]Since Ce oxide tends to introduce an oxygen deficiency especially, and it is stabilized and an oxygen-deficiency state can be held, it is an especially desirable oxide. If Ce oxide and Zr oxide are used together, the stability of an oxygen-deficiency state of Ce oxide will improve further. In this case, as for Ce oxide and Zr oxide, it is still more desirable to form the multiple

oxide or the solid solution. By considering it as a multiple oxide or a solid solution, still more oxygen deficiencies can be formed and the stability of an oxygen-deficiency state also improves further.

[0022]In order to form an oxygen deficiency in an oxide, the method of carrying out reduction processing of the oxide is illustrated. For example, the above-mentioned oxide What is necessary is just to process in a reducing gas air current in the temperature requirement of 100 °C - 800 °C for about 1 hour. A part of oxygen of an oxide combines with reducing gas, and it is removed because an oxide contacts reducing gas under an elevated temperature, and as a result, some oxides will be in an oxygen-deficiency state, and an oxygen deficiency can be introduced. It becomes difficult for a reduction reaction not to advance at less than 100 °C, but for reduction treatment temperature to form a desired oxygen-deficiency state. Treatment temperature. Since the specific surface area of an oxide will become small and catalytic activity will fall if it exceeds 800 °C, it is not desirable. It is also possible to carry out reduction processing using the reducing drugs represented by hydrazine, aluminum borohydride, etc.

[0023]As reducing gas used for reduction processing, hydrocarbon and aldehyde, such as methane besides reducing gas, such as hydrogen and carbon monoxide, etc. are mentioned. as the reducing gas concentration at the time of reduction processing -- 0.1 volume % - 100 volume % -- more -- desirable -- from 1 volume % 100 volume % is good.

[0024]And the quantity of an oxygen deficiency can be easily adjusted by adjusting the temperature of reduction processing, time, etc. by knowing beforehand the relation between the amount of active oxygen contained, and the quantity of an oxygen deficiency. For example, it is desirable to contain active oxygen 40 micro more than mol/g. A reaction with an environmentally harmful substance [in / that the content of active oxygen is 40 micro less than mol/g / ordinary temperature 50 °C or less] is not enough. If the amount of active oxygen is carried out more than ing and 40 micro mol /, oxidation reaction of an environmentally harmful substance will advance promptly, and the purification activity of the environmentally harmful substance in an ordinary temperature region will become very high. Although the oxidation purification of an environmentally harmful substance is [the elevated temperature over 50 °C] possible, since an oxygen deficiency may lose, it is desirable to use it in 10-40 °C more preferably 50 °C or less.

[0025]As the precious metals supported by the ordinary temperature catalyst of this invention, as being chosen out of Pt, Pd, Rh, Ir, Au, and Ru, a kind can be used as it is few. Among these, a kind may be sufficient and two or more kinds can also be supported. Especially high Pt of activity is desirable. As opposed to the oxide in which the oxygen deficiency was introduced as for the holding amount of these precious metals It is preferred to consider it as 0.1 to 10 % of the weight. At less than 0.1 % of the weight, since the catalytic activity in 50 °C or less is not acquired, it is not desirable. Even if it supports the precious metals exceeding 10 % of the weight, purification efficiency will not improve considering addition, but abundant use of the expensive precious metals will be carried out, and it becomes a cost hike.

[0026]The publicly known support methods, such as the adsorption supporting method, the evaporating method, and supercritical fluid technique, can be used for support of the precious

metals. And in order for the not less than 90% to support the precious metals with a particle state with a particle diameter of 2 nm or less, it can carry out easily by adjusting the specific surface area of the method of adjusting the firing condition after supporting as a precious-metals drug solution, or an oxide. When calcinating in the atmosphere, it is calcination temperature, for example. What is necessary is just to be 500 °C or less. In supporting, for example to a $\text{CeO}_2\text{-ZrO}_2$ solid solution, the specific surface area of a $\text{CeO}_2\text{-ZrO}_2$ solid solution

It is good to use the thing more than $100\text{-m}^2/\text{g}$. An oxygen deficiency can be more effectively introduced by supporting the precious metals, before carrying out reduction processing of the oxide, and carrying out reduction processing of it.

[0027]The composition of the ordinary temperature catalyst of this invention is concretely explained about the case where $\text{CeO}_2\text{-ZrO}_2$ used as a solid solution or a multiple oxide is hereafter used as an oxide.

[0028]After $\text{CeO}_2\text{-ZrO}_2$'s mixing the oxide powder of another side if needed and depositing it with a coprecipitation method, an alkoxide process, etc. using the solution which at least one side of a Ce compound and a Zr compound dissolved, it can be formed by calcinating it. The mixture of CeO_2 powder and ZrO_2 powder may be calcinated at an elevated temperature.

[0029]The mole ratio of Ce and Zr in $\text{CeO}_2\text{-ZrO}_2$ is Ce:Zr= 100:1-1. : The range of 100 is preferred, the range of Ce:Zr=20:1 - 1:10 is more preferred, and the range of Ce:Zr=5:1 - 1:1 is still more preferred. An oxygen-deficiency state is more maintainable to stability by considering it as this range. It is desirable to make molar quantity of Ce larger than the molar quantity of Zr. An oxygen-deficiency state can be formed more easily by this, and the amount of active oxygen can be made more.

[0030]One sort further chosen from the oxide of transition metals, such as the oxide of rare earth elements, such as Y, La, Nd, and Pr, Fe, Mn, Co, Cr, nickel, and Cu, as a third component may be included in $\text{CeO}_2\text{-ZrO}_2$. By blending these third components, the oxygen-deficiency state of $\text{CeO}_2\text{-ZrO}_2$ can be maintained still more stably. The content of this third component has preferred 1-30-mol thing to consider as % of the whole. The effect made to contain when less than this range is not acquired, but if it is made to contain exceeding 30-mol %, it will become difficult to form an oxygen deficiency.

[0031]In order to introduce an oxygen deficiency into $\text{CeO}_2\text{-ZrO}_2$, it can carry out by carrying out reduction processing using reducing gas, as described above. Thereby, an oxygen deficiency is mainly introduced into CeO_2 . in this case, percentage of n in CeO_n $1.5 \leq n < 2$ -- more -- desirable -- If it changes into the oxygen-deficiency state of the range of $1.5 \leq n \leq 1.8$, the effect excellent in especially purification of formaldehyde is shown. An n value. Less than 1.5 state is difficult to identify on the usual ultimate analysis conditions, though formation is considered to be difficult and has become so in the usual reduction processing. The oxygen-deficiency state of an oxide can be measured, for example according to an X diffraction etc. From the field of catalytic activity, it is from the surface of a catalyst particle from the inside of a

catalyst particle. Percentage in an about 100-nm surface It is desirable to consider it as the range of $1.5 \leq n \leq 1.8$.

[0032]as the precious metals supported by $\text{CeO}_2\text{-ZrO}_2$ -- Pt, Pd, Rh, Au, and Ru -- a kind is preferred at least and especially Pt is preferred. the holding amount of the precious metals -- $\text{CeO}_2\text{-ZrO}_2$ As opposed to 150 g 0.1g to 20 g -- more -- desirable -- It is preferred to be referred to as 0.5 to 5 g. In order to support the precious metals, it supports before reduction processing and reduction processing is performed after precious-metals support. when manufacturing $\text{CeO}_2\text{-ZrO}_2$ with a coprecipitation method etc., it was made to coprecipitate under coexistence of the precious metals -- it can calcinate back and can also support.

[0033]The catalyst of this invention is prepared as powdered, and can fabricate and use it for a pellet type. the surface of a honeycomb substrate -- a law -- a coated layer can also be formed from catalyst powder like a method.

[0034]

[Example]Hereafter, an example and a comparative example explain this invention concretely.

[0035](Example 1) CeO_2 powder (specific surface area $120\text{m}^2/\text{g}$) 150 g is impregnated with the specified quantity of the dinitrodiammine platinum solution of prescribed concentration, and it heats and evaporates to dryness after churning to it, and is in the atmosphere after that. It calcinated at 500 ** for 3 hours, and Pt was supported. The holding amount of Pt is CeO_2 powder. It is 2g to 150 g.

[0036]next, the obtained Pt support CeO_2 powder is arranged in the nitrogen air current 1 volume % containing CO -- reduction processing for 15 minutes was performed at 500 **, the oxygen deficiency was introduced, and the ordinary temperature catalyst Of Example 1 was prepared.

[0037](Example 2) The ordinary temperature catalyst of Example 2 was prepared like Example 1 except having used the $\text{CeO}_2\text{-ZrO}_2$ solid solution powder (specific surface area $120\text{m}^2/\text{g}$) of Ce:Zr=5:1 which replaced with CeO_2 powder and was manufactured with the coprecipitation method.

[0038](Example 3) Calcination temperature at the time of Pt support The ordinary temperature catalyst of Example 3 was prepared like Example 1 except having considered it as 300 **.

[0039](Comparative example 1) The ordinary temperature catalyst of the comparative example 1 was prepared like Example 1 except having used the $\text{CeO}_2\text{-ZrO}_2$ solid solution powder (specific surface area $30\text{m}^2/\text{g}$) of Ce:Zr=5:5 which replaced with CeO_2 powder and was manufactured with the coprecipitation method.

[0040](Comparative example 2) The ordinary temperature catalyst of the comparative example 2 was prepared like Example 1 except having used the CeO_2 powder (specific surface area $3\text{m}^2/\text{g}$) of low specific surface area.

[0041](Comparative example 3) Calcination temperature at the time of Pt support The ordinary

temperature catalyst of the comparative example 3 was prepared like Example 1 except having considered it as 700 **.

[0042](Comparative example 4) Calcination temperature at the time of Pt support The ordinary temperature catalyst of the comparative example 4 was prepared like Example 1 except having considered it as 800 **.

[0043](Comparative example 5) Calcination temperature at the time of Pt support The ordinary temperature catalyst of the comparative example 5 was prepared like Example 1 except having considered it as 900 **.

[0044](Comparative example 6) It replaced with the dinitrodiammine platinum solution and the ordinary temperature catalyst of the comparative example 6 was prepared like Example 1 except having used Pt colloidal solution by which particle diameter was controlled by about 5 nm.

[0045](Comparative example 7) It replaced with the dinitrodiammine platinum solution and the ordinary temperature catalyst of the comparative example 7 was prepared like Example 1 except having used Pt colloidal solution by which particle diameter was controlled by about 10 nm.

[0046](Comparative example 8) It replaced with the dinitrodiammine platinum solution and the ordinary temperature catalyst of the comparative example 8 was prepared like Example 1 except having used Pt colloidal solution by which particle diameter was controlled by about 15 nm.

[0047](Comparative example 9) The coconut husks activated carbon (specific surface area $700\text{m}^2/\text{g}$) generally used as adsorption material was made into the comparative example 9.

[0048]The particle diameter of Pt currently supported was measured about the catalyst of <examination / evaluation> (example 1 of examination) examples 1-3, and the comparative examples 1-8. Those average value was computed by transmission electron microscope observation having mainly performed measurement of Pt particle diameter, and having performed simultaneously measurement by CO amount of adsorption, and measurement by an X diffraction to others. A result is shown in Table 1.

[0049]5g of catalysts of Examples 1-3 and the comparative examples 1-8 have been arranged to the evaluation system, respectively, the model gas which consists of CO concentration [of 250 ppm] and O₂ concentration 20 volume % and remainder N₂ was passed by a part for 10 l. of gas mass flow/, and the CO conversion in a room temperature (25 **) was measured. A result is shown in Table 1.

[0050]And the relation between Pt particle diameter of Table 1 and CO conversion is plotted, and a result is shown in drawing 1.

[0051]

[Table 1]

	酸化物		Pt薬液	焼成温度 (°C)	Pt粒径 (nm)	CO転化率 (%)
	種類	比表面積(m ² /g)				
実施例 1	CeO ₂	120	ジニトロジ・アソミPt	500	1.2	95
実施例 2	CeO ₂ - ZrO ₂	120	ジニトロジ・アソミPt	500	1.7	90
実施例 3	CeO ₂	120	ジニトロジ・アソミPt	300	1.1	93
比較例 1	CeO ₂ - ZrO ₂	30	ジニトロジ・アソミPt	500	5.4	50
比較例 2	CeO ₂	3	ジニトロジ・アソミPt	500	20	15
比較例 3	CeO ₂	120	ジニトロジ・アソミPt	700	10	19
比較例 4	CeO ₂	120	ジニトロジ・アソミPt	800	15	15
比較例 5	CeO ₂	120	ジニトロジ・アソミPt	900	25	10
比較例 6	CeO ₂	120	Ptコロイド* (約 5nm)	500	5	40
比較例 7	CeO ₂	120	Ptコロイド* (約10nm)	500	10	13
比較例 8	CeO ₂	120	Ptコロイド* (約15nm)	500	15	7

[0052]From Table 1 and drawing 1, the catalyst of each example is 2 nm or less in Pt particle diameter. And if Pt particle diameter is 2 nm or less, not less than 90% and the very high thing of CO conversion in ordinary temperature are clear, and it turns out that the catalytic activity in ordinary temperature is falling, so that Pt particle diameter becomes large.

[0053](Example 2 of an examination) the inside of the 5-l. well-closed container filled up with the atmosphere which chooses the adsorption material of the catalyst Of Example 1, and the comparative example 9, and contains 900 ppm of methyl mercaptans -- respectively -- 0.1g is put in and, Aging of the methyl mercaptan concentration in the well-closed container in room temperature (25 **) atmosphere was measured by the gas chromatography. A result is shown in drawing 2.

[0054]It is clearer than drawing 2 the catalyst's of Example 1 to excel the adsorption material of the comparative example 9 in the elimination characteristics of methyl mercaptan, and it turns out that it has high ordinary temperature purification activity.

[0055](Example 3 of an examination) The adsorption material of the catalyst of Example 1 and the comparative example 9 was chosen, and aging of triethylamine concentration and ethylene concentration was measured like the example 2 of an examination except having used the atmosphere which replaces with methyl mercaptan and contains triethylamine or 900 ppm of ethylene, respectively. A result is shown in drawing 3 and drawing 4.

[0056]It is clearer than drawing 3 and drawing 4 the catalyst's of Example 1 to excel the adsorption material of the comparative example 9 in the elimination characteristics of triethylamine and ethylene, and it turns out that it has high ordinary temperature purification

activity.

[0057]

[Effect of the Invention] That is, according to the ordinary temperature catalyst of this invention, decomposition removal of the environmentally harmful substances, such as CO, amines, and formaldehyde, can be efficiently carried out at ordinary temperature 50 ** or less.

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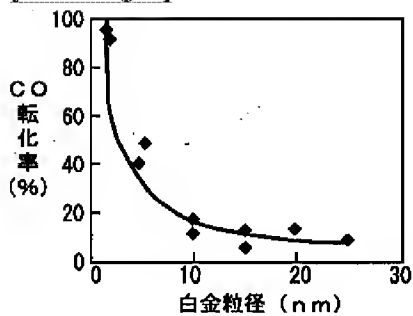
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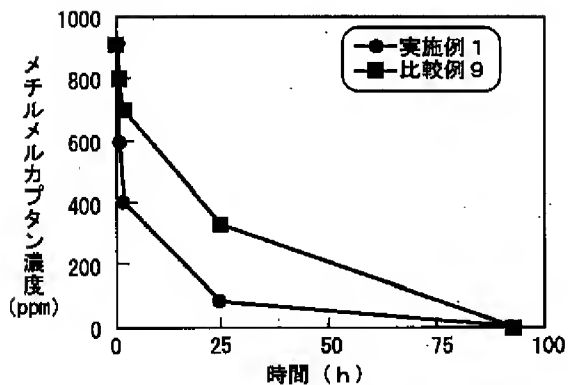
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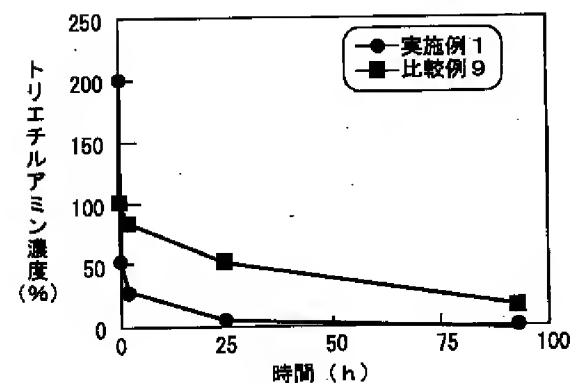
[Drawing 1]



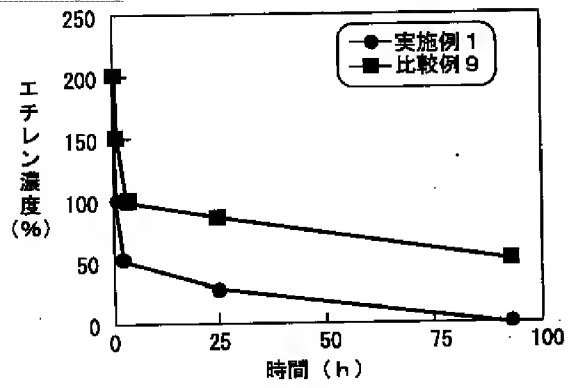
[Drawing 2]



[Drawing 3]



[Drawing 4]



[Translation done.]